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THE INFLUENCE OF ISOTHERMAL OXIDATION PARAMETERS ON THE TRIBOLOGICAL PROPERTIES OF TITANIUM

WPŁYW PARAMETRÓW UTLENIANIA IZOTERMICZNEGO NA WŁAŚCIWOŚCI TRIBOLOGICZNE TYTANU

Key words: titanium, thermal oxidation, oxide layers, tribological properties.

Abstract The paper presents the results of tests concerning the tribological properties of titanium Grade 2 subjected to thermal oxidation at a temperature of 600°C and 700°C for 72 hours. The morphology of the obtained oxide scale was determined using a scanning electron microscope. After oxidation at 600°C, the resultant oxides concentrated mostly on the roughness elevations formed during the grinding of samples. On raising the temperature to 700°C, finer and more agglomerated oxide particles were formed. Tribological tests have shown that titanium Grade 2 in a non-oxidised condition is characterised by very poor resistance to sliding wear. It has been found that the presence of an oxide layer on the surface of titanium significantly improves its poor tribological properties. Oxide layers obtained at temperatures of 600°C and 700°C allowed obtaining as much as a triple reduction of volumetric wear. Analysis of the morphology of the wear trace surface has shown the presence of corrugation wear on a non-oxidised specimen in the form of two alternate regions with different morphologies. It has been demonstrated that oxide layers obtained during thermal oxidation eliminate the phenomenon of corrugation wear.

Słowa kluczowe: tytan, utlenianie termiczne, warstwy tlenkowe, właściwości tribologiczne.

Streszczenie W pracy przedstawiono wyniki badań dotyczące właściwości tribologicznych tytanu Grade 2 poddanego procesowi utleniania termicznego w temperaturze 600 i 700°C w czasie 72 h. Na skaningowym mikroskopie elektronowym określono morfologię otrzymanej zgorzeliny tlenkowej. Po utlenianiu w temperaturze 600°C powstałe tlenki koncentrowały się głównie na wzniesieniach nierówności powstałych w trakcie procesu szlifowania próbek. Podwyższenie temperatury do 700°C prowadziło do powstawania drobniejszych, skupionych cząstek tlenków. Badania tribologiczne wykazały, że tytan Grade 2 w stanie nieutlenionym charakteryzuje się bardzo słabą odpornością na zużycie ścierne. Stwierdzono, że obecność warstwy tlenkowej na powierzchni tytanu w sposób znaczący poprawia jego słabe właściwości tribologiczne. Warstwy tlenkowe otrzymane w temperaturze 600 i 700°C pozwoliły uzyskać redukcję zużycia objętościowego nawet 3-krotnie. Badania morfologii powierzchni śladów wytarcia wykazały występowanie zużycia falistego na próbce nieutlenionej w postaci dwóch naprzemianległych obszarów o różnej morfologii. Wykazano, że warstwy tlenkowe uzyskane w procesie utleniania termicznego skutecznie eliminują zjawisko zużycia falistego.

INTRODUCTION

Titanium and its alloys are characterised by high biocompatibility and resistance to the destructive nature or corrosion processes, due to the formation of passive layers. The self-forming oxide layer has good adhesion and a thickness of the order of a few nanometres **[L. 1, 2]**. The passive layer ensures good corrosion resistance, but it does not effectively protect the surface of the material against, e.g., tribological wear, which is a particularly important problem in the case of titanium and its alloys used in medicine. To change the thickness of oxide layers, different surface modification techniques are applied, which enable obtaining oxide layers characterised by varied structure, morphology, thickness, as well as chemical and phase composition **[L. 2, 3]**. The properties of oxide layers have a significant impact on tribological and corrosion durability, and they play an important role in the interactions with the surrounding environment **[L. 4–6]**.

One of the methods that facilitate the formation of oxide layers with different thicknesses on titanium and its alloys is the thermal oxidation process conducted in the

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air atmosphere. This method utilises the low resistance of titanium to oxidation and the phenomenon of oxygen diffusion at higher temperatures, thereby allowing hardening of the upper layer by creating a relatively thick TiO_2 film over the oxygen diffusion zone **[L. 3, 7, 8]**. This titanium surface shows an increased resistance to sliding wear, as a result of the formation of a crystalline titanium oxide layer (rutile). According to the authors of paper **[L. 9]**, the use of thermal oxidation allows a significant improvement of the poor tribological properties of titanium and its alloys. This method allows a reduction of wear of 400% to 600%.

This study addresses issues related to the determination of the effect of oxidation temperature on the morphology and resistance to sliding wear of oxide layers formed on the titanium surface as a result of single stage thermal oxidation.

EXPERIMENTAL PROCEDURES

The material used for tests was a 40 mm diameter rod made of titanium Grade 2. Specimens were prepared from the rod, which had the form of discs, 40 mm in diameter, and 5 mm in thickness. The surface of the specimens was mechanically ground with SiC abrasive paper with a gradation of 600, 1200, and 2500. The oxidation process was conducted in a laboratory chamber furnace at temperatures of 600 and 700°C for 72 h. After soaking at the given temperature and time, the specimens were removed from the furnace and cooled in the air.

Observation of the surface morphology of the obtained oxide layers was conducted using a JEOL JSM 6480 scanning electron microscope with the following magnifications: 1000x, 2000x, 5000x, and 7000x. The observations were performed on specimens intended for tribological tests, oxidised at 600 and 700°C for 72 h.

Tests of sliding wear resistance were performed using a tribometer (TRB) from Anton-Paar in a ball-on-disk system. Disks with a 40 mm diameter made of titanium Grade 2, covered and not covered with oxide layers, were used in the tests. Balls made of Al_2O_3, 6 mm in diameter were used as counter-specimens. The tests were carried out with the following parameters: load 5N, sliding speed – 0.1 m/s, and friction distance – 1000 m. For each tested case, 4 repetitions were made. The tests were performed in an air-conditioned room at an ambient temperature of 21 ±1ºC and humidity of 50 ±5%. As part of the tests, the volumetric wear and friction coefficient of the interacting frictional couple were determined. The volumetric wear of the disk was calculated according to the following formula:

$$V_v = \frac{V}{F \cdot s} \tag{1}$$

where

- V_V – volumetric wear, $mm^3/N{\cdot}m$,
- F – load applied (normal), N,
- s – friction distance, m,
- V – average volume of the material removed during tribological wear, calculated from the formula: $V = P{\times}2\pi r$, mm^3,
- P – average area of the removed material, mm^2,
- r – working radius of the friction distance, 15 mm.

Measurements of geometrical parameters of the formed wear traces were taken using the Mitutoyo SJ-500 surface roughness tester.

Analysis of the surface morphology of the wear traces formed after tribological tests was performed on the JEOL JSM-6480 scanning electron microscope at magnifications ranging from 100 to 7000x.

RESULTS AND DISCUSSION

Morphology of the surface of oxide layers

Results of the observation of surface morphology of the oxide layers obtained on titanium Grade 2 at temperatures of 600 and 700°C are shown in **Fig. 1**. Tests of surface morphology have demonstrated that oxidation conducted at a temperature of 600°C enabled covering the entire investigated surface, but in a non-uniform manner. The obtained oxides concentrated mostly on the roughness elevations formed during the grinding of specimens, as evidenced by the surface topography similar to that of the non-oxidised sample. It is possible to observe the direction of grinding in the microscopic images, which is connected with the insignificant thickness of the oxide layer (<1 μm). An increase in the oxidation temperature to 700°C leads to obtaining a completely different surface morphology. The layer formed is distinguished by the presence of fine oxide particles. The grinding direction is no longer visible in the microscopic images, which testifies to a greater thickness of the oxide layer (ca. 6 μm) compared to the case where the oxidation temperature was 600°C. A similar surface morphology was achieved in paper **[L. 10]**, when oxidising titanium alloy Ti-6Al-4V at a temperature of 700°C for 4 h.

Tests of resistance to sliding wear

Results of tribological tests conducted in conditions of technically dry friction are presented in **Figs. 2–4**. **Figure 2** presents the friction coefficient values obtained for titanium Grade 2 subjected to and not subjected to isothermal oxidation.

Based on the analysis of the test results, it was found that titanium Grade 2 not subjected to oxidation was distinguished by a high friction coefficient value of ca. 0.65, which is consistent with the results presented in paper **[L. 11]**. Covering of the surface of titanium Grade 2 with 2 oxide layers contributes to increasing the friction coefficient value, which is at variance with

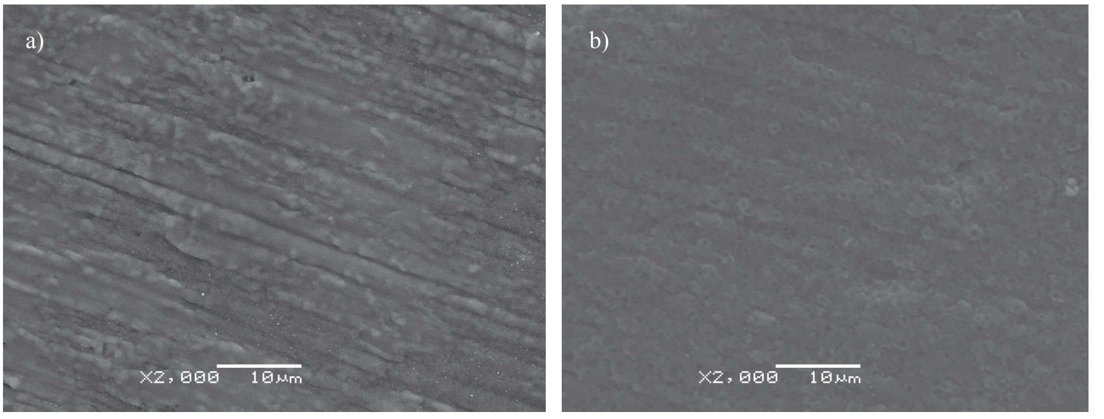

Fig. 1. Surface morphology of the oxide layer obtained on titanium Grade 2 at 600°C (Fig. a) and 700°C (Fig. b)
Rys. 1. Morfologia powierzchni warstwy tlenkowej otrzymanej na tytanie Grade 2 w temperaturze 600 (**Rys. a**) i 700°C (**Rys. b**)

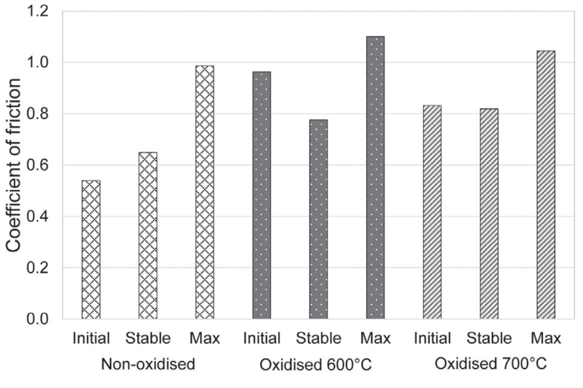

Fig. 2. Friction coefficient for the non-oxidised and oxidised titanium Grade 2 at temperatures of 600 and 700°C
Rys. 2. Współczynnik tarcia dla nieutlenionego oraz utlenionego tytanu Grade 2 w temperaturze 600 i 700°C

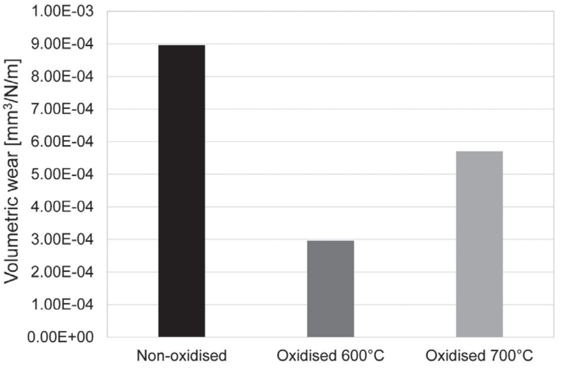

Fig. 3. Volumetric wear of titanium Grade 2 before and after thermal oxidation at 600 and 700°C for 72h
Rys. 3. Zużycie objętościowe tytanu Grade 2 przed i po utlenianiu termicznym w temperaturze 600 i 700°C w czasie 72 h

some reference data **[L. 4, 11]**. This may be related to the increased roughness of the surface after oxidation (Ra = 0.1 µm before oxidation, Ra = 0.15–0.24 µm after oxidation). An increase of the friction coefficient was particularly observed at the initial stage of the tribological interaction. It was found that the friction coefficient increased by 20% for the surface oxidised at 600°C, and by 26% for the surface oxidised at 700°C.

Figure 3 presents the results of volumetric wear examinations determined for the non-oxidised and oxidised surface. It was found that the greatest volumetric wear was present on the surface that was not subjected to oxidation. It was also demonstrated that thermal oxidation leads to a considerable improvement of the tribological properties of titanium Grade 2. The highest resistance to sliding wear was exhibited by the oxide layer formed at a temperature of 600°C, which allowed increasing the resistance to sliding wear by 300%. The oxide scale obtained at 700°C did not ensure as good resistance to sliding wear as the layer obtained at 600°C, although it also contributes to the improvement of the tribological properties.

Figure 4 shows the results of measurements of the depth and width of wear traces left after tribological tests. The trace left after oxidation at 600°C has the smallest width; however, it is a little deeper than the trace formed on the specimen after oxidation at 700°C. Nevertheless, this does not change the fact that the lowest value of the volumetric wear parameter was obtained for the oxidation variant at 600°C. It was affirmed that, as the oxidation temperature increased, the depth of wear traces decreased. The layer formed at 700°C was characterised, in turn, by the widest trace of wear, which could have resulted from the poor adhesion of the upper part of the oxide layer, due to which it underwent partial delamination. This phenomenon can also explain the deterioration of the tribological properties compared to the oxide layer formed at a temperature of 600°C.

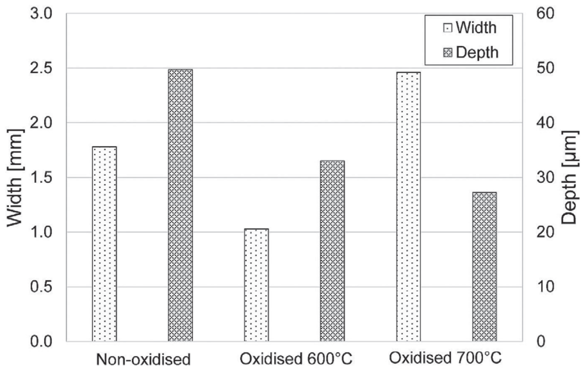

Fig. 4. The width and depth of wear traces after tribological tests

Rys. 4. Szerokość i głębokość śladów wytarcia po badaniach tribologicznych

Morphology of wear traces after tribological tests

Figures 4 and **5** present the morphology of the wear traces after tribological tests of non-oxidised specimens and specimens oxidised at temperatures of 600 and 700°C.

Based on microscopic observations, a diverse morphology of the working surface of specimens was found after tests of resistance to sliding wear. The so-called corrugation wear phenomenon was observed on the non-oxidised surface, which was distinguished by characteristic, alternate areas in a dark and light colour. The wear products are accumulated in the dark area **(Fig. 5a)**, while in the light colour area, the wear products are present in trace quantities; therefore, numerous deep scratches are visible, which formed after the tribological interaction **(Fig. 5b)**. The length of the light colour area is clearly greater than that of the dark colour area.

The oxide layers obtained after thermal treatment at 600°C and 700°C allowed complete elimination of the corrugation wear phenomenon. At the same time, numerous scratches with varied depths and fine wear products were observed on the friction working surface. They were formed after tribological interaction. It was shown that the wear trace after oxidation at a temperature of 700°C was characterised by more gentle scratches compared to the specimen oxidised at 600°C. This may be connected with a greater width of the wear trace, which ensured the distribution of the load over a larger area during tribological tests. The obtained results of microscopic observations are consistent with the results of the tribological tests.

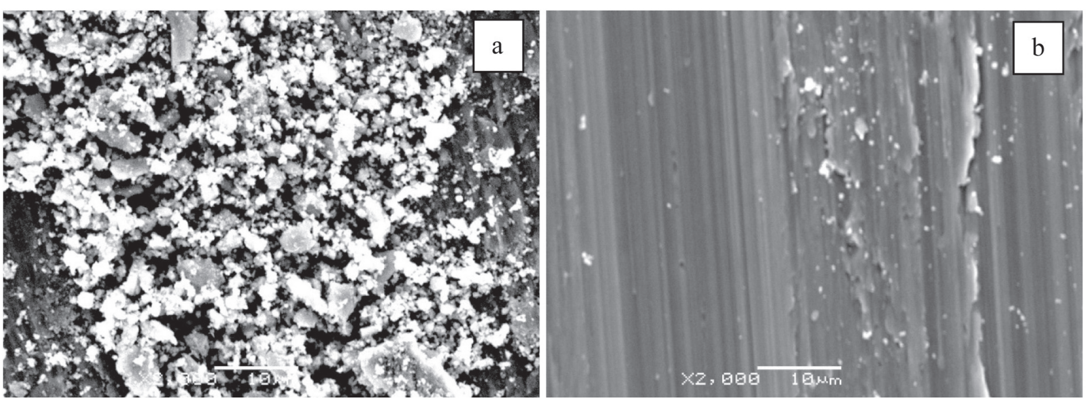

Fig. 5. Surface morphology of the wear trace along with areas formed as a result of corrugation wear (a – dark area, b – light area)

Rys. 5. Morfologia powierzchni śladu wytarcia wraz z obszarami powstałymi w wyniku zużycia falistego (a – obszar ciemny, b – obszar jasny)

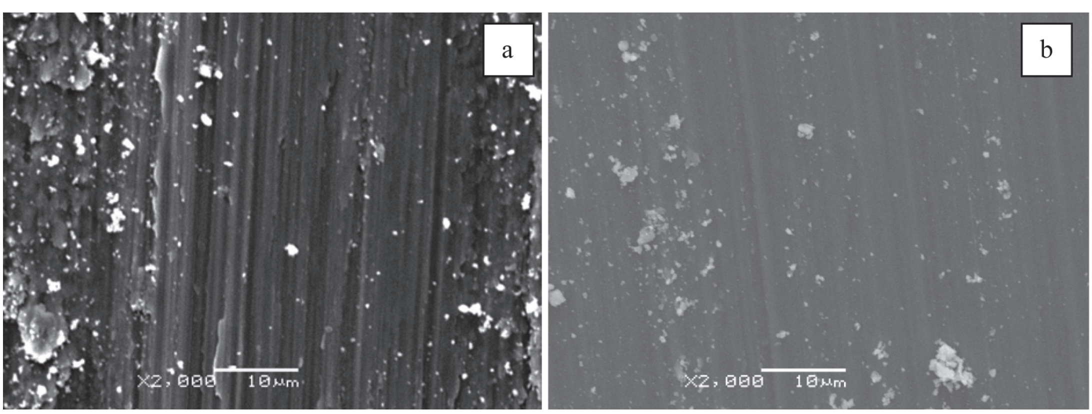

Fig. 6. Surface morphology of the wear traces after tribological tests for specimens oxidised at 600 (Fig. a) and 700°C (Fig. b)

Rys. 6. Morfologia powierzchni śladów wytarcia po badaniach tribologicznych próbek utlenionych w temperaturze 600 (**Rys. a**) i 700°C (**Rys. b**)

CONCLUSIONS

Based on the conducted analysis of the test results, the following conclusions can be formulated:

1. Examination of the morphology of the oxide layers showed that the oxide scale obtained at a temperature of 600°C covered the examined surface unevenly, in a manner similar to the surface topography before the oxidation process. At a temperature of 700°C, a uniform layer was formed, consisting of fine agglomerated oxide particles.
2. The presence of oxide layers on the surface of titanium Grade 2 allowed, to a large degree, the improvement of tribological properties of this titanium. The best resistance to sliding wear was shown by the layer obtained at 600°C (a triple reduction in volumetric wear compared to the non-oxidised surface).
3. The presence of oxide layers on the surface of titanium did not cause a reduction of the friction coefficient. At the initial stage of the tribological interaction, an increase in its value was observed.
4. SEM observations of the wear traces that occurred following the tribological interaction with an Al_2O_3 ball showed, for the non-oxidised specimen, the presence of alternating, morphologically varied areas which had formed as a result of corrugation wear. At the same time, numerous scratches with varied depths and fine wear products were observed on the friction working surface.
5. The results of tribological tests indicate that oxide layers obtained via isothermal oxidation, apart from improving resistance to sliding wear, allow the effective elimination of the adverse phenomenon of corrugation wear on titanium Grade 2.

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